Diffusion Controlled Electron Transfer of Horse Spleen Ferritin at Polypyrrole Modified Gold Electrodes

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Ferritin is a protein found in most organisms, whose principal function is to sequester excess iron in the cell. Its other functions are to store the iron, and to supply it wherever it is needed, such as in the synthesis of other iron-containing proteins. When iron, as Fe (II), enters the protein it is oxidized to Fe (III). Before iron can leave the protein shell, it must first be reduced to Fe (II). Thus, ferritin's functions of iron uptake and release involve redox reactions, however, the details of the mechanisms are not well understood.

Electrochemical methods are well suited for investigating the redox reactions of proteins. The direct electron transfer of ferritin in the adsorbed state has been demonstrated at bare gold, gold modified with adsorbed layers of mercaptoethane derivatives, and tin-doped indium oxide electrodes. However, diffusion-controlled electron transfer of ferritin has not yet been observed. It is possible that ferritin adsorbs onto electrode surfaces, forming a layer which precludes the electron transfer of dissolved ferritin. Data obtained from diffusion-controlled voltammetric experiments can be used to evaluate the electron transfer properties of ferritin under conditions that more closely resemble those in biological systems. For example, ferritin is closer to its native state in the dissolved state than in the adsorbed state. An effort has been made to find an electrode system onto which ferritin does not strongly adsorb, yet is capable of promoting the direct electron transfer of ferritin.

Unsubstituted pyrrole was polymerized at gold electrodes. The performance of the modified electrodes were evaluated using ferrocyanide in KCl. The electrode was placed into horse spleen ferritin in pH 7.0 phosphate buffer containing KCl. The cyclic voltammogram, starting at 0.20 V (vs. Ag/AgCl) and scanning between 0.20 and -1.0 V, gave a fairly well defined current-potential curve with a midpoint potential of -0.10 V and a peak potential difference of 365 mV (at 5 mV/sec sweep rate), indicating a quasi-reversible process. The peak current varied linearly with the square root of the scan rate indicating a diffusion controlled process. Further characterization includes pH, ionic strength, and concentration dependencies.

The results suggest that ferritin may not be so strongly adsorbed to the polypyrrole surface so as to inhibit the electron transfer of dissolved species. However, the current-potential behavior does suggest that the interaction between ferritin and polypyrrole is one that promotes direct electron transfer.

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